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UV Absorbers and Wavelength Shifters

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IMPROVING DYE LASER EFFICIENCY WITH UV ABSORBERS AND WAVELENGTH SHIFTERS

by

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The nonuniform heating in flashlamp pumped dye lasers forms refractive index gradients in the dye solution. These gradients distort the wavefront of the laser beam resulting in limited output power, limited pulse repetition rate, and limited attainable linewidth (1).

The absorbed flashlamp radiation is converted to heat in two processes described by the following equations (2):

$$Q_1(r, z, t, \lambda) = C \epsilon(\lambda)(1 - \phi)I(r, z, t, \lambda)$$

$$Q_2(r, z, t, \lambda) = C \epsilon(\lambda) \phi \left(1 - \frac{\lambda}{\lambda_{\max}} \right) I(r, z, t, \lambda)$$

where: c = molar concentration of dye

$\epsilon(\lambda)$ = molar extinction coefficient

ϕ = quantum yield of dye

$\lambda_{\max}$ = wavelength of maximum absorption

$I(r, z, t, \lambda)$ = intensity of pump radiation

Here Q_1 is the heat arising from radiationless deactivation of the fraction $(1 - \phi)$ of absorbed photons. Q_2 is the heat arising from the loss of absorbed photon energy due to Stoke's shift. The total heat power absorbed per unit

volume, $Q(r, z, t)$, is the sum of these two contributions integrated over the absorption band of the dye (3).

$$Q(r, z, t) = \int_{\text{abs. band}} c \epsilon(\lambda) \left(1 - \frac{\phi\lambda}{\lambda_{\text{max}}} \right) I(r, z, t, \lambda) d\lambda$$

The temperature increase at any time is obtained by integrating $Q(r, z, t)$ up to time t . The change

$$\Delta T(r, z, t) = \frac{1}{\rho_o c_p} \int_0^t Q(r, z, t') dt'$$

where:

ρ_o = solvent density

c_p = solvent specific heat

in refractive index with temperature is directly related to $\Delta T(r, z, t)$.

$$n(r, z, t) - n_o = \left(\frac{\partial n}{\partial T} \right)_{\rho_o} \Delta T(r, z, t)$$

Values of $\Delta T(r, z, t)$ for a 10^{-4} M Rhodamine 6G solution in ethanol were calculated for three absorption band ranges 350 - 590 nm, 450 - 570 nm, and 490 - 500 nm. These are plotted in Figure 1. The three curves represent the heat accumulation for each absorption band range after a time of 10^{-6} seconds, which is about the time duration of the pump pulse. The important thing to note is that the heat accumulation is much lower for the 490 - 500 nm band. This is the region of strong absorption by Rhodamine 6G as shown in Figure 2. Light is absorbed before it penetrates deeply, and then is fluoresced efficiently leaving very little heat behind. The other regions of the absorption band such as 350 - 490 nm (deep

penetration and no fluorescence) cause severe solution heating.

Flashlamp radiation covers a broad spectral range (4). Because much of the radiation may contribute to heating, it would be useful to either eliminate light of detrimental wavelengths with filters or shift it to wavelengths which pump the laser dye with minimal heating. The triaxial flashlamp dye cell system shown in Figure 3 lends itself well to modification of pump light by either filtering or wavelength shifting methods. UV absorbers or wavelength shifters could be dissolved in the coolant which circulates in the annular region between the flashlamp and the dye. These compounds would decrease the heating, protect the dye from UV induced photodecomposition, and enable the pump radiation to be used more efficiently. UV absorbing compounds would simply absorb the UV radiation before it reaches the dye cell. Wavelength shifters would absorb flashlamp radiation on the short wavelength side of the dye absorption band and then fluoresce in the absorption band of the laser dye.

Twelve UV absorbers and twelve wavelength shifters have been evaluated for use as possible pump light filters. They are listed in Tables I and II. The evaluation was based on absorption spectra, resistance to photodegradation under simulated flashlamp pumped laser conditions, and, where applicable, fluorescence spectra. The photodegradation tests were carried out using an ILC linear xenon flashlamp L 484 LCT 953 pulsed at 2 Hz at 5 KV. Solutions of each compound at about 10^{-3} M concentration were placed in a glass tube surrounding the flashlamp to provide maximum exposure to the radiation.

The selection of the appropriate UV absorber or wavelength shifter to be used in conjunction with a given laser dye is based on the absorption spectrum of the dye. If a UV absorber is needed, then the compound should be chosen so that its long wavelength absorption peak is just to the short wavelength side of the absorption peaks of the laser dye. If a wavelength shifter is needed, then the compound should be chosen so that there is maximum overlap between the fluorescence spectrum of the shifter and the absorption spectrum of the dye. For instance perylene absorbs strongly from 390 to 440 nm, but wastes pump light below 390 nm. Tinopal 5BM (Table II) would be an excellent wavelength shifter for perylene because it absorbs the short wavelengths (below 390 nm) and reradiates the light at 430 nm, in the strong absorption region for perylene. Tinopal 5BM is also very resistant to photodecomposition. The data from Tables I and II can be used to select protectors and shifters for other dyes.

LITERATURE CITED

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FIGURE CAPTIONS

FIGURE

- 1 Temperature change in milidegrees as a function of distance from the center of a 1.00 cm diameter cylindrical dye laser cell. Three different bands of wavelengths for the flashlamp are plotted. Thermal lensing effect is proportional to the slope of the line.
- 2 Absorption spectrum of 10^{-4} M Rhodamine 6G in ethanol.
- 3 Cross-section of a triaxial dye laser. Channels are cylindrical and coaxial. Flash occurs in outer channel; coolant and wavelength shifter flow in intermediate channel; and laser dye solution flows in inner channel.

FIG. 1

RHODAMINE 6G
IN ETHANOL

FIG. 2

FIG. 3

TABLE I. Absorption Peaks and Photodecomposition Half-Lives of Selected UV Absorbers.

<u>Compound</u>	<u>Wavelength; nm; (log ϵ)</u>	<u>Solvent</u>	<u>Approximate photo-decomposition half-life</u>
phenyl salicylate	274(3.56), 227(4.26)	EtOH	~1 hr
2,2',4,4'-tetrahydroxy-benzophenone	351(4.19), 286(4.05), 243(3.97)	EtOH	~12 hrs
2,2'-dihydroxy-4,4'-dimethoxybenzophenone	353(4.15), 285(4.14), 249(4.05)	EtOH	~12 hrs
2,4-dihydroxybenzophenone	324(4.00), 290(4.13), 243(4.09)	EtOH	>16 hrs
2-hydroxy-4-methoxy-benzophenone	326(3.91), 292(4.11), 241(4.00)	EtOH	~12 hrs
Uvinol MS40	328(4.27), 288(4.17), 243(4.13)	EtOH	~16 hrs
Tinuvin P	338(4.20), 297(4.15), 242(4.02)	EtOH	~12 hrs
Tinuvin 320	342(4.20), 303(4.19), 245(3.86)	EtOH	~12 hrs
Tinuvin 327	350(4.23), 311(4.18), 252(3.88)	EtOH	~12 hrs
Cyasorb UV 1988	314(4.41), 230(4.05), 208(4.05)	EtOH	~ 1.25 hrs
Uvinol N-35	303(4.04), 224(4.03)	EtOH	~2.5 hrs

TABLE II. Absorption and Fluorescence Peaks, and Photodecomposition
Half-Lives of Selected Wavelength Shifters.

Compound	Solvent	Absorption peaks λ in nm	Fluorescence peaks λ in nm	Approximate photon decomposition half-life
Leucophor B	H ₂ O	347,277	445	>12 hrs
Tinopal RBS	EtOH	363	430	~ 2 hrs
Tinopal CBS	H ₂ O	350	435	~ 1 hr
Tinopal 5BM	EtOH	332,269	430	~12 hrs
Tinopal AMS	EtOH	331,272	430	~12 hrs
PFF	EtOH	325	366	~.5 hr
PFO	EtOH	304	362,378	~.5 hr
α -NPO	EtOH	330	398	~.5 hr
PED	EtOH	302	362	4 hrs
BEOT	EtOH	374	435	1 hr
Bis MSB	EtOH	346	396,420	1 hr
Cumarin 4	EtOH	324	390	1 hr